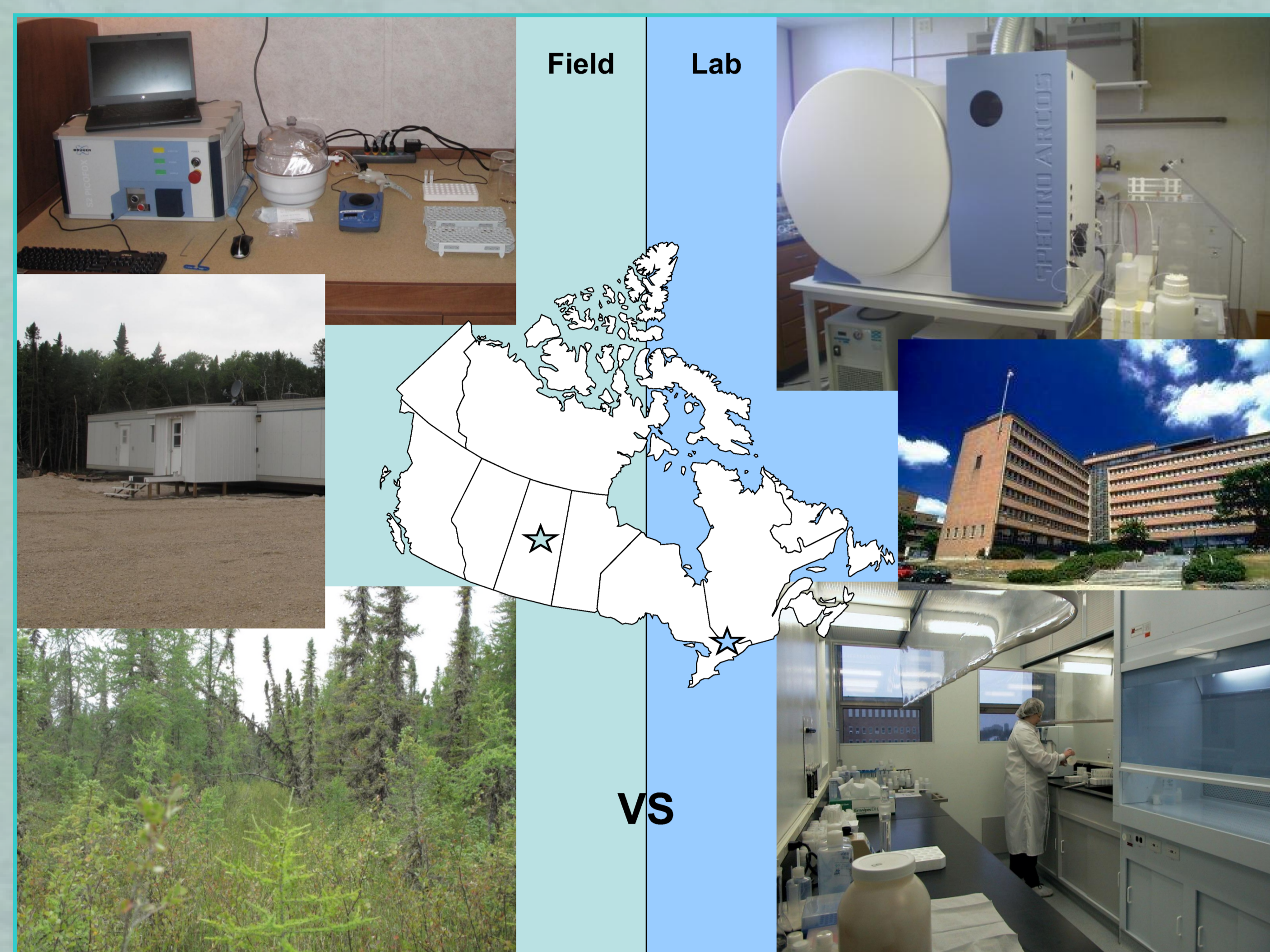


INTRODUCTION

For many geochemical studies, the very low detection limits of Inductively Coupled Plasma (ICP) technology are less important than the time delay and high costs associated with laboratory-based analysis. Total reflection X-ray fluorescence spectroscopy (TXRF), with on-site analyses at low ppb level detection limits, offers a potential compromise. To test whether this is a suitable field technology, the Geological Survey of Canada's TGI4 Program, in conjunction with the Inorganic Geochemical Research Laboratory (IGRL), deployed a TXRF Spectrometer (Bruker AXS – S2 Picofox) and a small field laboratory to a remote field location in Saskatchewan.



LOGISTICS

- A remote field laboratory set-up in a bedroom of a prospecting camp
- Electricity, running water, constant temperature ~20°C
- Humidity within instrumental tolerances
- Camp sitting on crushed rock requirement for contamination control procedure!
- Lights inside facility, but extra mobile lighting was required
- Camp location close to sampling sites

CONTAMINATION CONTROL

An experiment was designed to assess the contamination level of the field laboratory environment on the sample disk used to dry and carry the water sample for analysis. Pre-cleaned blank TXRF sample carrier quartz disks were used for the experiment. From the first part of Table 1, one can see that the blank quartz disks are initially very clean. These same disks were left beside the TXRF instrument face up without covering them. Each day, elemental determination was performed on one disk to obtain the maximum amount of contamination collected for that period of time. Another test was performed by wiping the dust from the sample disk after 96 h exposure to determine whether the contamination could effectively be removed.

Preventive measures to minimize the effect of contamination:

- Limit the amount of traffic in the room.
- Clean the workbench with a damp cloth each day.
- Create a clean sample handling zone with Kimwipe™ delicate surface wipers.
- Cover disk either in a desiccator, under a beaker, a Kimwipe™ or in a plastic bag.
- Move the samples by transporting them in a plastic bag.
- Monitor contamination via the analysis of a control blank quartz disk exposed to the environment in the same manner as the samples

TABLE 1: Contamination Control

	Ambient Time of Exposure (hour)	Condition of Exposure	S	K	Ca	Mn	Fe	Sr
			TXRF Absolute ng	TXRF Absolute ng	TXRF Absolute ng	TXRF Absolute ng	TXRF Absolute ng	TXRF Absolute ng
QTZ D1	0	unprotected	< 0.1	< 0.1	< 0.1	< 0.001	< 0.02	< 0.001
QTZ D2	0	unprotected	< 0.1	< 0.1	< 0.1	< 0.001	< 0.02	< 0.001
QTZ D3	0	unprotected	< 0.1	< 0.1	< 0.1	< 0.001	< 0.02	< 0.001
QTZ D4	0	unprotected	< 0.1	< 0.1	< 0.1	< 0.001	< 0.02	< 0.001
QTZ D5	0	unprotected	< 0.1	< 0.1	< 0.1	< 0.001	< 0.02	< 0.001
QTZ D1	24	unprotected	0.6	1.3	5.4	0.026	1.07	0.006
QTZ D2	48	unprotected	0.8	2.0	12.0	0.063	1.77	0.013
QTZ D3	72	unprotected	1.5	3.9	18.7	0.114	3.59	0.022
QTZ D4	96	unprotected	2.4	4.7	22.2	0.285	4.85	0.028
QTZ D5	96	unprotected + wiped	< 0.1	0.3	< 0.1	< 0.001	0.03	< 0.001
QTZ DC	0	protected	< 0.1	< 0.1	< 0.1	< 0.001	< 0.02	< 0.001
QTZ DC	24	protected	< 0.1	< 0.1	< 0.1	< 0.001	< 0.02	< 0.001
QTZ DC	48	protected	< 0.1	< 0.1	< 0.1	< 0.001	< 0.02	< 0.001
QTZ DC	72	protected	< 0.1	< 0.1	< 0.1	< 0.001	< 0.02	< 0.001
QTZ DC	96	protected	< 0.1	< 0.1	< 0.1	< 0.001	0.03	< 0.001

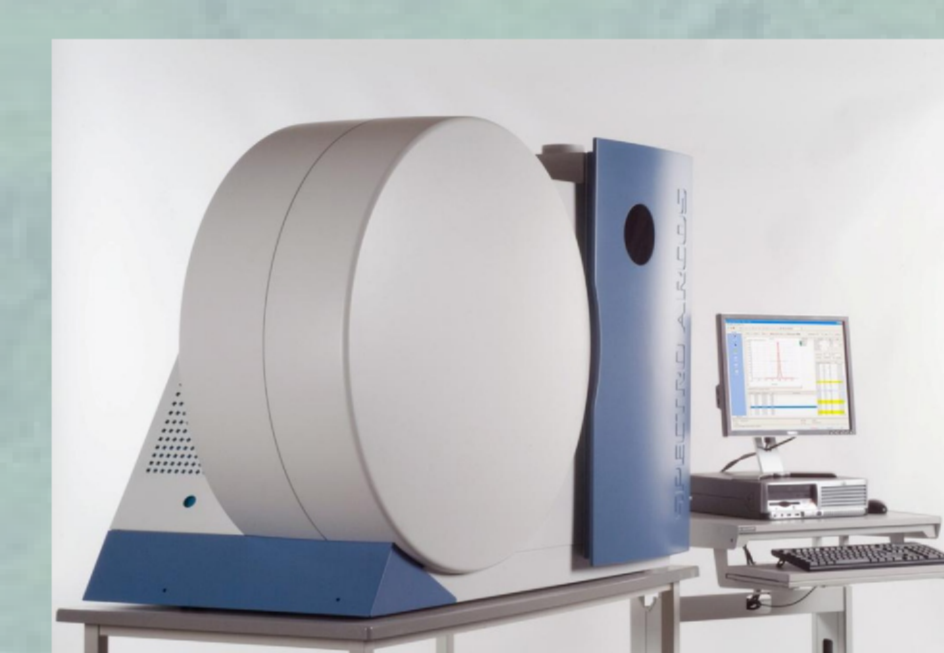
INSTRUMENTATION

Bruker AXS - S2 PICOFOX TXRF



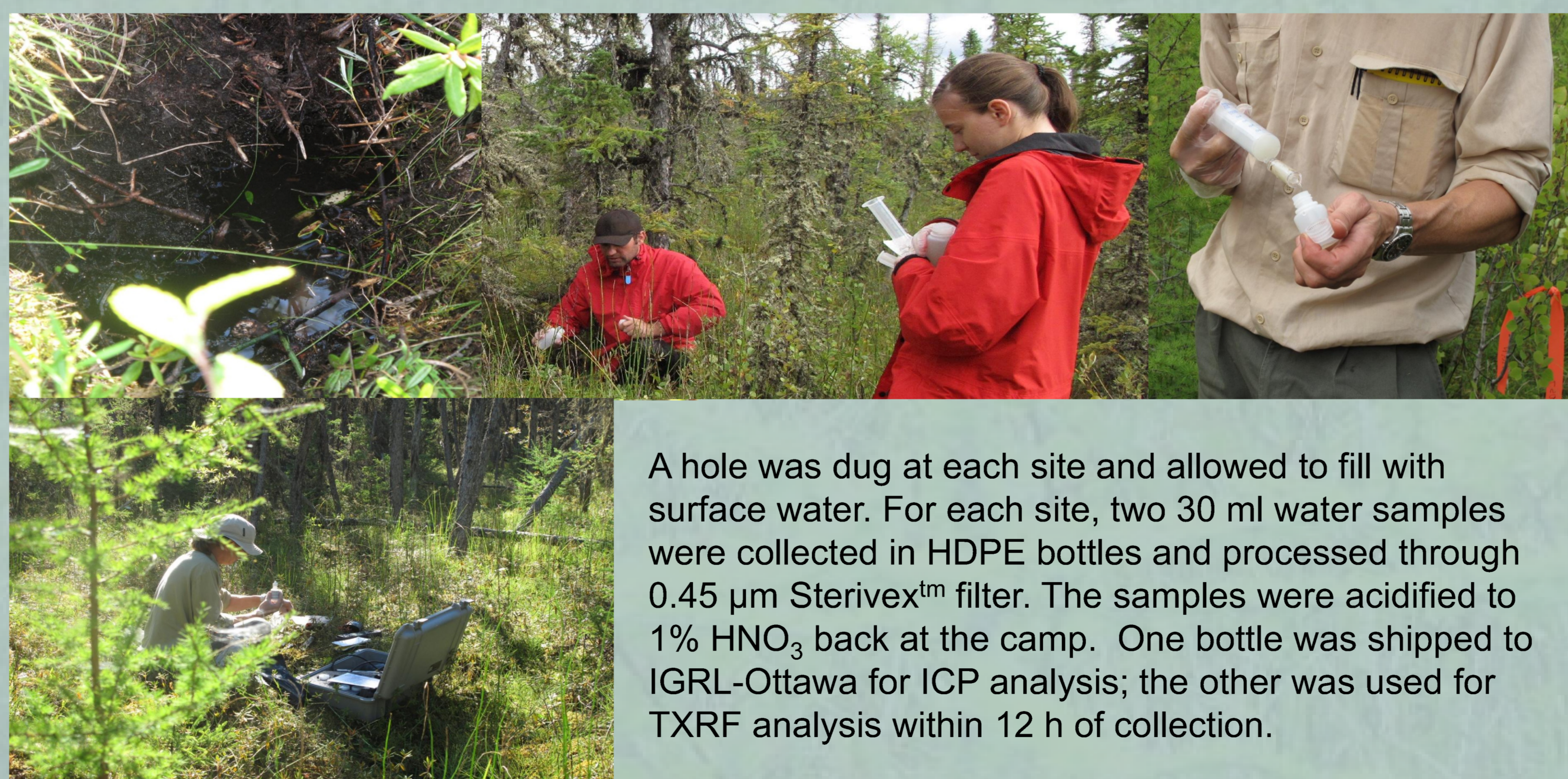
- Molybdenum (Mo) X-ray tube
- Ni/C multilayer monochromator
- XFlash silicone drift detector (SSD) with an effective area of 30 mm²
- Measurements made with the Mo-K α excitation (17.48eV) for 1000 s live time at 50 kV and 600 μ A
- Deconvolution of the spectrum using Bruker's SPECTRA7 software

Spectro Arcos ICP-OES



- End on plasma (axial) viewing
- Burgener Miramist nebuliser
- Sample uptake 1ml/min
- G.E. Helix Cyclonic spray chamber
- Forward power 1500W
- Plasma 14.5 lpm
- Auxiliary 0.9 lpm
- Nebuliser 0.8 lpm
- Buffer 1% CsNO₃ (1 : 5 with sample)

FIELD COLLECTION



A hole was dug at each site and allowed to fill with surface water. For each site, two 30 ml water samples were collected in HDPE bottles and processed through 0.45 μ m Sterivex™ filter. The samples were acidified to 1% HNO₃ back at the camp. One bottle was shipped to IGRL-Ottawa for ICP analysis; the other was used for TXRF analysis within 12 h of collection.

METHODOLOGY

An aliquot of the sample was taken within a few hours of collection to prepare for TXRF quantitative analysis. 1 ml of sample was thoroughly mixed with 10 μ l of a Ga solution (10 mg/L). 10 μ l from this solution was transferred onto a polished quartz sample carrier disk and dried in a vacuum desiccator. The disk was analysed as soon as the sample was dried.

ICP analysis was performed 3 months later at IGRL-Ottawa. A Spectro Arcos EOP ICP-OES was calibrated with newly prepared matrix matched multi-element standards. Certified Reference Materials and drift monitors were inserted in the analytical sequence for QA/QC. Analysis was performed on 4 ml splits of the original samples.

TXRF vs. ICP COMPARISON

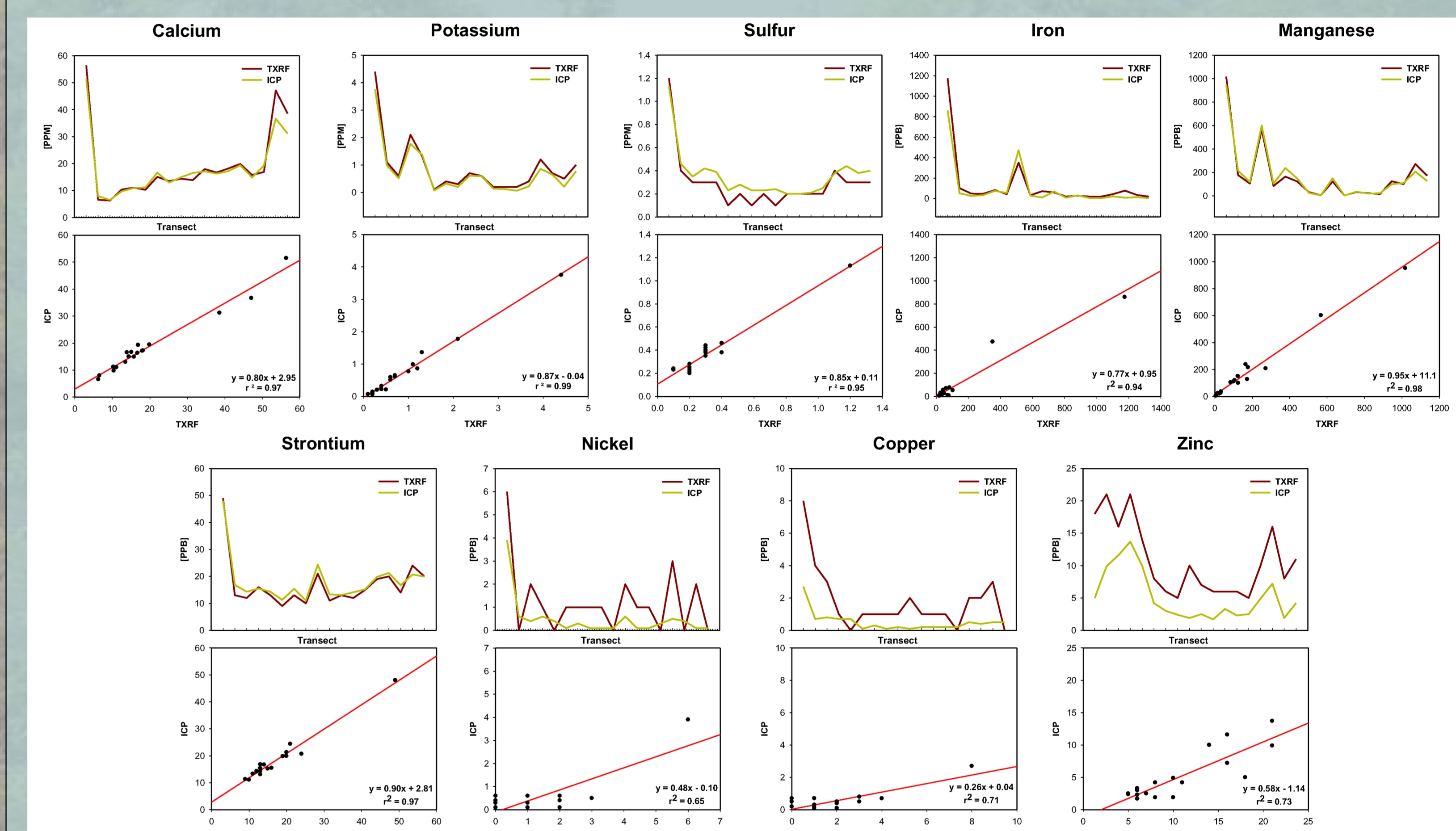


FIGURE 1: Element profiles for a field transect (25 m spacing) and TXRF vs. ICP-OES correlations

- Correlation between TXRF and ICP data is excellent ($R^2 = 0.94-0.99$) for elements well above the limit of detection (LOD); e.g. Ca, Fe, K, Mn, S and Sr.
- TXRF values are consistently higher than ICP-OES values. These biases (5-20%) suggest that TXRF factory calibration needs adjustment.
- For many trace elements, TXRF vs. ICP correlations are also good, but most concentrations are close to or below LOD making quantification uncertain, e.g., Cu, Ni.
- For Zn a severe bias is observed, plus potential contamination effects, making the TXRF quantification unreliable. This is interpreted to be the result of an interference (Figure 2).

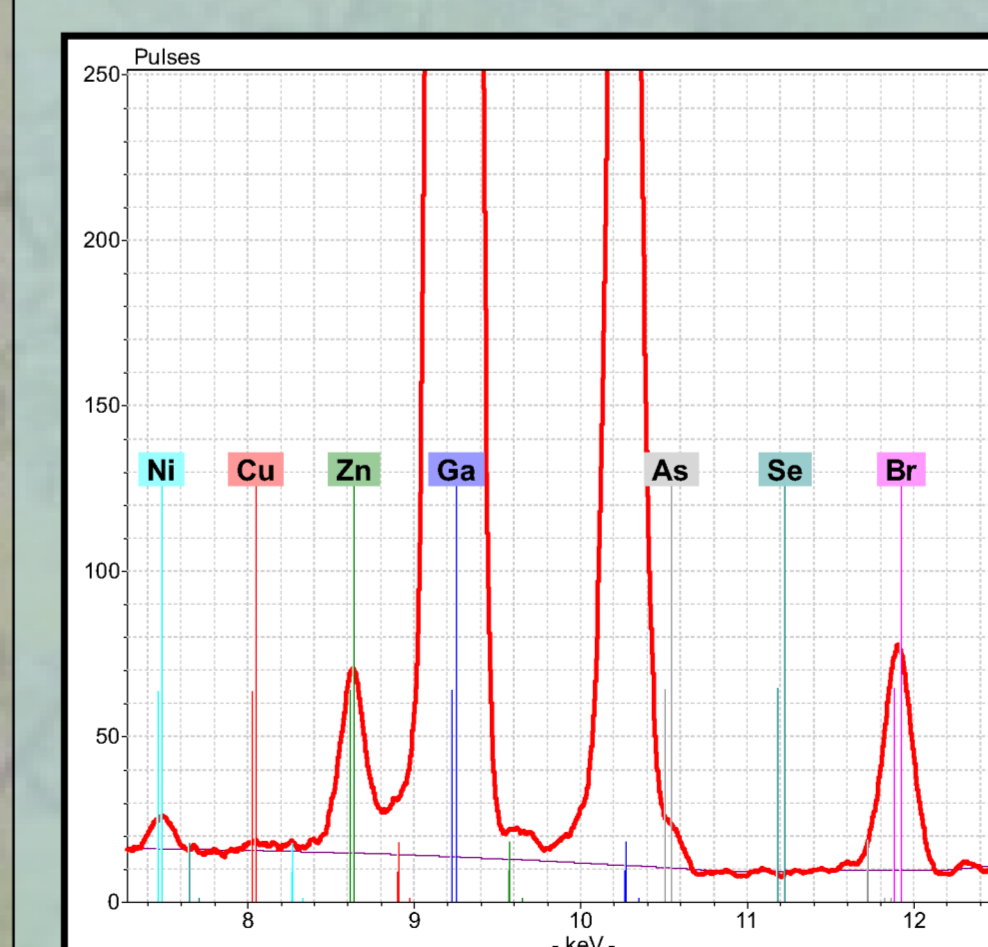


FIGURE 2: Zn Spectrum

- The internal standard, Ga, is at high concentration relative to Zn, which is close to LOD.
- Tails of the Ga K α (9.251eV) and K β (10.267eV) lines partially overlap the Zn K α (8.637eV) and K β (9.570eV) lines.
- Ga – Zn spectrum deconvolution may not provide accurate correction of the interference.
- Solution: recalibrate the TXRF and/or use Se as an internal standard instead of Ga

CONCLUSION

A TXRF instrument was successfully deployed in the field. The sampling and analytical protocol indicates that careful attention to detail makes TXRF analysis a valid method for field-based trace element analysis at low ppb levels.